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INFINITE

Aerospace composites digitally sensorized
from manufacturing to end-of-life

D2.2
Magnetic microwires, manufacture and testing

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ABSTRACT / EXECUTIVE SUMMARY	
Abstract	In this report we describe the manufacturing magnetic wires to be used as sensor elements in carbon fibre NCF reinforcement composites and the testing results.
Keywords	Glass-coated microwires, fabrication, testing.

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1. INTRODUCTION

INFINITE aims to develop sensors and analyser based on the usage of ferromagnetic microwires to be embedded in aerospace composite structural parts, in order to monitor manufacturing and structural health throughout the whole life cycle of the component.

This deliverable represents the work as performed in WP2 Sensor system development **of INFINITE project, a R&I project funded by HORIZON-CL5-2021-D5-01-06 that will last for three years.** This task is part of work package 2 which focuses on the Sensor system development. The overall objective of WP2 is to manufacture magnetic wires to be used as sensor elements in carbon fibre NCF reinforcement composites, to design a portable sensor element reader system, to develop calibration processes and to develop models to aid in the calibration procedure as well in predicting sensor sensitivities and interpreting the sensor signal response.

The purpose of this document is to provide the description of magnetic microwire manufacturing and testing, and describe the actions performed within 14 months.

Glass-coated amorphous microwires are prepared by the Taylor-Ulitovsky technique. Such microwires have several features making them suitable for many applications in composite monitoring: micrometric diameters (between 0.5 and 100 µm), thin, insulating, biocompatible and flexible glass-coating, as well as good magnetic softness and superior mechanical properties [1-3]. However, magnetic properties are affected by several factors, such as chemical composition of metallic alloy, microstructure or even the geometry (metallic nucleus diameter, d, and total diameter D)

The INFINITE project aims to develop the advanced sensing technology for the aerospace sector and demonstrate the capability for the integration of embedded microwire in structural carbon composite parts. Particularly, several challenges have been found during the project development. Thus, the surrounding conductive carbon fibers interfere in the microwave signal generated by ferromagnetic microwires, making it difficult to be measured.

Consequently, during first 14 months of the project development magnetic microwires of several compositions and geometries have been manufactured and tested.

2. MAGNETIC MICROWIRES MANUFACTURING

Glass-coated microwires used for the project have been prepared by the Taylor-Ulitovsky method described elsewhere [1-3].

The preparation method (commonly referred to as the modified Taylor-Ulitovsky method or the quenching and drawing method) consists of simultaneous rapid quenching of a composite microwire (a metallic nucleus inside a glass capillary) from the melt when it passes through a stream of coolant (water or oil) (see Fig. 1a) [1-3].

The most modern facility for the glass-coated microwire preparation (available in Tamag) is provided with a feedback system that allows one to control the main manufacturing parameters and the microwire geometry (metallic nucleus diameter, *d*, and the total microwire diameter, *D*) using a sensor that measures the impedance during the preparation process (see Fig. 1b).

In the first step, an ingot of a metal alloy (usually a few grams) with a selected chemical composition is placed in a glass (Pyrex or Duran -like) tube inside a high frequency (typically 350-500 kHz) inductor heater. Then a droplet is formed upon heating the alloy above the melting point. The end of the glass tube adjacent to the melting metal alloy softens and covers the metal droplet. Then, a glass capillary is pulled out of the softened glass, which is caught by the rotating pick-up spool. The molten metal alloy fills the glass capillary and thus forms a glass-coated microwire, the metallic nucleus of which is completely covered with a continuous thin and flexible glass coating (see Fig. 1a). The glass tube is moved at a uniform feed rate of 0.1 to 10

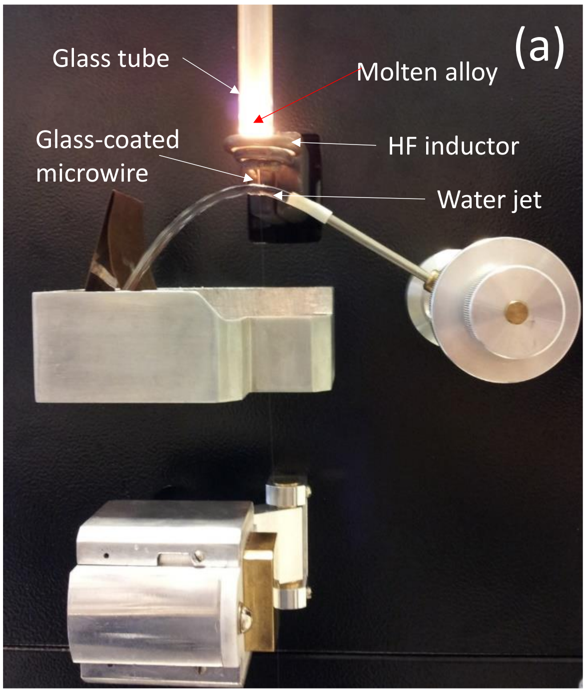

Fig.1. Schematic picture of the Taylor–Ulitovsky

mm/min to ensure a continuous process.

The metallic nucleus diameter, *d*, is determined by the speed at which the wire is drawn, increasing as it decreases, while the glass-coating thickness depends mainly on the feed rate of the glass tube, increasing as it increases.

The formed wire is cooled by a stream of coolant (water or oil) at a distance of about 1 cm under the high frequency inductor. Such coolant allows to increase the quenching rate and thus to prepare microwires with amorphous structure.

Typical metallic nucleus diameters of glass-coated microwires are between 5 and 30 µm. However, for the signal increasing we needed to increase the metallic nucleus diameters up to about 40 µm.

On the other hand, the Taylor-Ulitovsky process consists in the simultaneous rapid solidification of a metal nucleus inside a glass coating.

It is commonly recognized that the internal stresses, σ_i, arising from different thermal expansion coefficients of a glass coating and a metallic alloy are the largest [1-3]. The value of such internal stresses is affected by the microwire geometry: glass-coating thickness, metallic nucleus diameter, *d*, and total microwire diameter, *D*. In the most simplified approximation σ_i has been expressed as [1,2]:

$$\sigma_\phi = \sigma_r = P = \varepsilon E k \Delta/(k/3+1)\Delta + 4/3; \ \sigma_z = P(k+1)\Delta + 2/(k\Delta+1) \qquad (1)$$

where σ_ϕ, σ_r and σ_z are circular, radial and axial stresses, respectively, $\Delta=(1-\rho^2)/\rho^2$, $k=E_g/E_m$, E_m, E_g- Young modulus of metallic nucleus and glass, respectively, $\varepsilon=(\alpha_m-\alpha_g)(T_m-T_{room})$, α_m, α_g are thermal expansion coefficients of metallic nucleus and glass, respectively, and T_m, T_{room} are melting and room temperatures. It means that internal stresses depend mainly on the difference of thermal expansion coefficients and on ρ-ratio ($\rho=d/D$). The more detailed theoretical estimations give σ_i values up to 4 GPa [2]. Although internal stresses are distributed in a complex way, the important point is that the axial internal stresses are the largest ones [2]. The axial stresses and azimuthal stresses are positive (tensile) in most part of the metallic nucleus volume (roughly up to $d \sim 0.85\ D$) [1]. While, the radial internal stresses retain their sign and are positive (tensile).

3. MAGNETIC MICROWIRES TESTING

During WP1 several types of microwires with different compositions have been fabricated by Tamag and tested in the University of Basque Country (UPV/EHU) laboratory. The main aim at first approximation was to choose the microwire composition and geometry with the best microwave response.

The microscope Axio Scope A1 is a modular system that allows studying the material using several methods of contrast. Such microscope we used for the metallographic and geometry analysis of glass-coated microwires (in reflected and transmitted light).

Several images of glass-coated microwires prepared for the project development are provided in Fig.2.

Magnetic and magnetoimedance (GMI) testing is performed using the experimental facilities of the UPV/EHU.

Hysteresis loops have been measured using the fluxmetric method previously successfully employed by the UPV/EHU for studies of magnetic microwires [1,4]. The schematic picture of the experimental set-up is provided in Fig. 3.

The electromotive force, ϵ, in the pick-up coil with N turns produced by the change of magnetic flux, ϕ, is given by [4]:

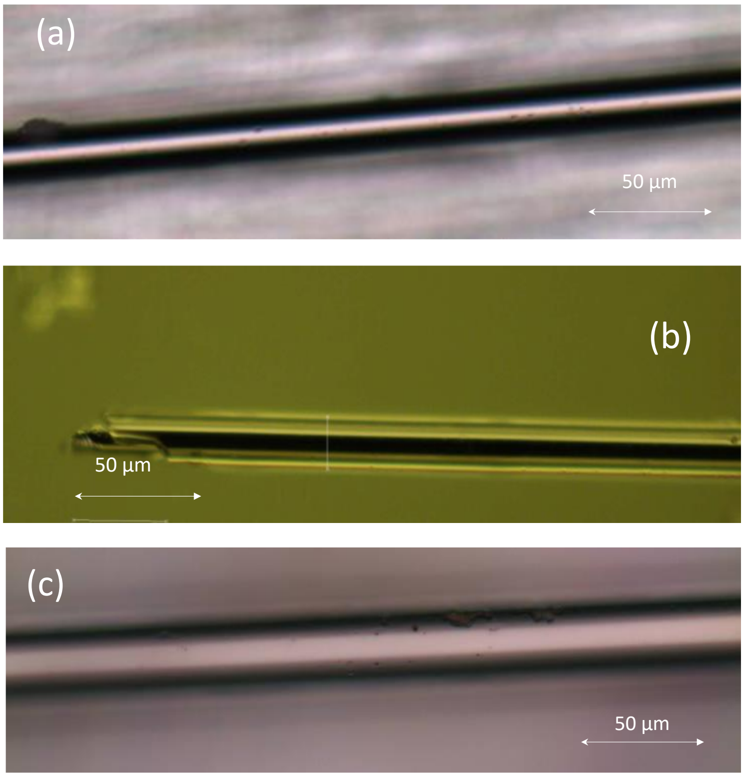

Fig.2. The images of the glass-coated microwires made by optical microscope Axio Scope A1.

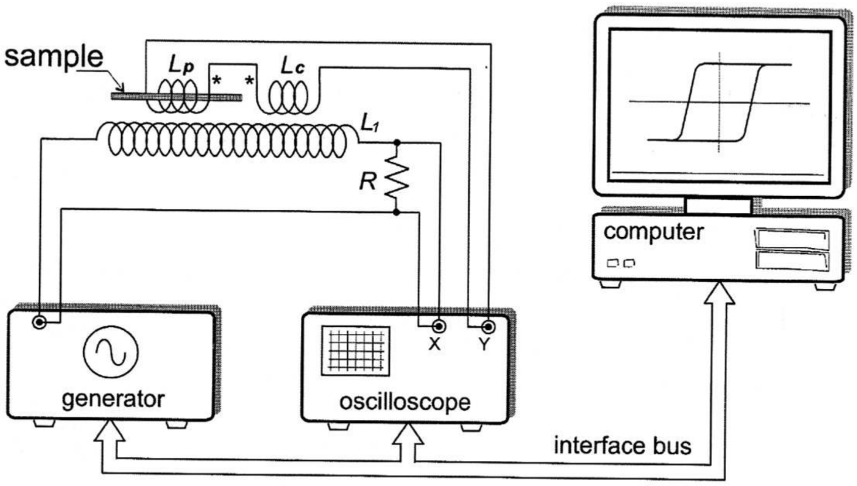

Fig.3 Scheme of the set-up available in the laboratory of UPV/EHU allowing measuring of hysteresis loops of magnetic microwires.

$$\epsilon = -N\frac{d\phi}{dt} \qquad (2)$$

The microwire occupies a small part of the coil cross-section. Therefore, the magnetic flux produced by the external field can be essentially relevant and hence it is necessary to consider both parts of magnetic flux: originating from the sample magnetization, *M,* and from the magnetic field, *H*:

$$\phi = \mu_0\,[(A_c - A_s)H + A_s(H + M)] = \mu_0[A_c\,H + A_s\,M] \quad (3)$$

where A_c and A_S are the coil and sample cross-section areas. Then, the induced voltage contains two components in pick-up coil.

$$\epsilon = -\,\mu_0 N\frac{d(A_c H + A_s\,M)}{dt} = -\mu_0\,N\,\left[A_c\frac{dH}{dt} + A_s\frac{dM}{dt}\right] \qquad (4)$$

An identical compensation coil is used to eliminate the component $A_c\,(dH/dt)$ due to an external magnetic field. The compensation coil is connected in series-opposition with the pick-up coil. Therefore, the resulting electromotive force, ϵ_c, depends only on the rate of change of the magnetization of the sample as following:

$$\epsilon_c = -\,\mu_0\,N\,A_s\frac{dM}{dt} \qquad (5)$$

As a result, ϵ_c = 0 in the absence of a sample. Then, the sample magnetization can be obtained by integrating the induced voltage as following:

$$M = \frac{1}{N\mu_0 A_s}\int \epsilon\, dt \qquad (6)$$

The hysteresis loops can be measured at different frequencies, *f*, however, usually *f* = 100 Hz is most useful. Hysteresis loops have been represented as the normalized magnetization, M/M_o, versus the applied magnetic field, *H*, where M_o is the magnetic moment of the sample at the maximum magnetic field amplitude, H_o [4]. In this way, the comparison of the hysteresis loops of microwires with different compositions (and hence different saturation magnetization) is more illustrative.

Additionally, DC hysteresis loops have been measured using PPMS device (available in UPV/EHU).

Various excitation and measurement methods are required to reveal the impedance matrix elements. The longitudinal and circumferential electrical field on the wire surface can be measured as voltage drop along the wire v_w and voltage induced in the pickup coil v_c wound on it [5,6].

$$v_w \equiv e_z l_w = (\varsigma_{zz} h_\varphi - \varsigma_{z\varphi} h_z) l_w \qquad (7)$$

$$v_c \equiv e_\varphi l_t = (\varsigma_{\varphi z} h_\varphi - \varsigma_{\varphi\varphi} h_z) l_t \qquad (8)$$

where l_w is the wire length, $l_t = 2\pi r N_2$ the total length of the pickup coil turns N_2 wounded directly on the wire.

The methods for revealing the different elements of impedance tensor are shown in Fig. 4. The longitudinal diagonal component ς_{zz} is defined as the voltage drop along the wire and corresponds to impedance definition in classical model (Fig. 4a,b)

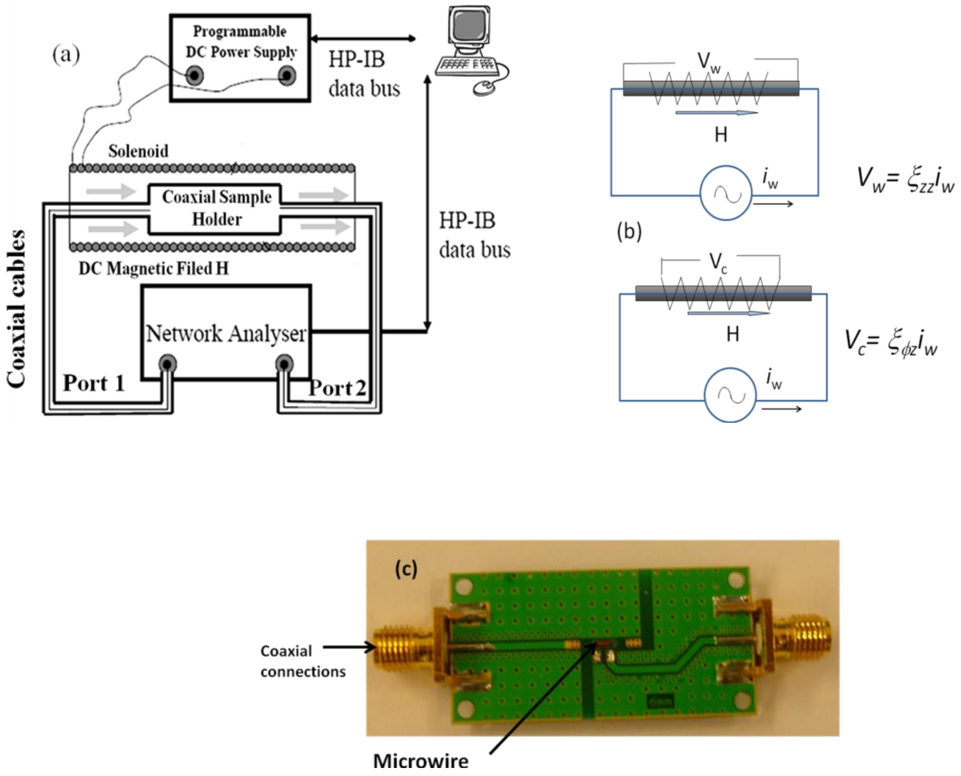

Fig.4. Schematic picture of the experimental set-up for measurements of GMI effect available in the laboratory of UPV/EHU (a), principles for revealing of the diagonal, ς_{zz}, and off-diagonal, $\varsigma_{z\varphi}$, impedance matrix elements (b) and the image of the micro-strip line (c).

$$\varsigma_{zz} \equiv \frac{v_w}{h_\varphi l_w} = \left(\frac{2\pi r}{l_w}\right)\left(\frac{v_w}{i_w}\right) \qquad (9)$$

The off-diagonal components $\varsigma_{z\varphi}$ and $\varsigma_{\varphi z}$ and the circumferential diagonal component $\varsigma_{\varphi\varphi}$ arose from cross sectional magnetization process ($h_\varphi \to m_z$ and $h_z \to m_\varphi$) [5,6].

Use of specially designed micro-strip sample holder (see Fig. 4c) placed inside a sufficiently long solenoid allows measuring of the magnetic field dependence of sample impedance, Z, using vector network analyzer from the reflection coefficient S_{11} using the expression:

$$Z = Z_0(1+S_{11})/(1-S_{11}), \qquad (10)$$

where Z_0=50 Ohm is the characteristic impedance of the coaxial line [5]. Described technique allows measuring of the GMI effect in extended frequency, *f*, ranges up to GHz frequencies.

The GMI ratio has been defined as:

$$\Delta Z/Z = [Z(H) - Z(H_{max})] / Z(H_{max}), \qquad (11)$$

where *H* is the applied axial *DC*-field with a maximum value, H_{max}, up to a few kA/m.

In amorphous microwires, the magnetoelastic anisotropy, K_{me}, together with the shape anisotropy, are the key factors that determine the character of the hysteresis loops. K_{me} is given by [1]:

$$K_{me} = 3/2\lambda_S\sigma \qquad (12)$$

where λ_s – the magnetostriction coefficient and $\sigma = \sigma_i + \sigma_{app}$ - total stresses, σ_{app} - applied stresses.

The λ_s sign and value of amorphous materials is primary influenced by the chemical composition [1].

In previous studies was demonstarted that the magnetostriction coefficient, λ_s, is primary affected by the compostion of the microwires. Vanishing λ_s (about 10^{-7}) is predicted in $(Co_{1-x}Fe_x)_{1-y}(Si\text{-}B\text{-}C)_y$ amorphous alloys at $0.05 \leq x \leq 0.1$ and $0.15 \leq y \leq 0.30$ [2]. Therefore, at the beginning we fixed the chemical compostion of ferromagnetic nucleus as $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ and $Co_{69}Fe_{3.6}Ni_1B_{12.8}Si_{10.7}Mo_{1.5}C_{1.2}$.

Such microwires have been prepared with different diameters: metallic nucleus diameter, d, ranging between 22 and 38 µm.

For comparison we prepared and measured magnetic properties of Fe-rich microwires ($Fe_{77.5}B_{15}Si_{7.5}$) with high and positive λ_s (about 40 x10^{-6}).

Experimental results on testing of manufactured microwires (magnetic characterization) are provided below.

1. Glass-coated microwires with the composition $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$, and following diameters: d≈22 µm, D ≈24µm.

In Fig. 5 the hysteresis loops of these microwires obtained using the flux-metric method are shown. $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires present rather soft magnetic properties with a coercivity, H_c, about 16 A m^{-1} and a magnetic anisotropy field, H_k, about 150 A m^{-1}.
In Fig. 6 are provided the results on GMI effect of these microwires.

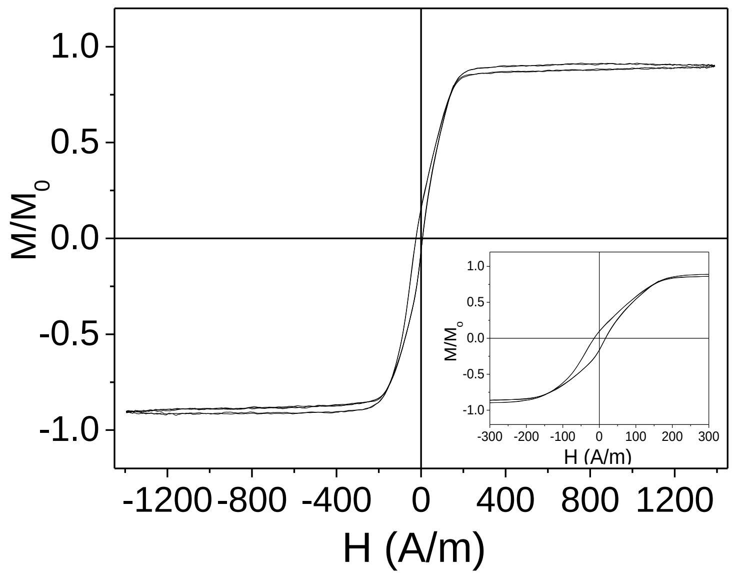

Fig.5. Hysteresis loops as-prepared $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires (d≈22 μm, D≈24μm).

As evidenced from Fig. 6, $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires present high GMI effect (maximum GMI ratio is about 175 % at 200 MHz).

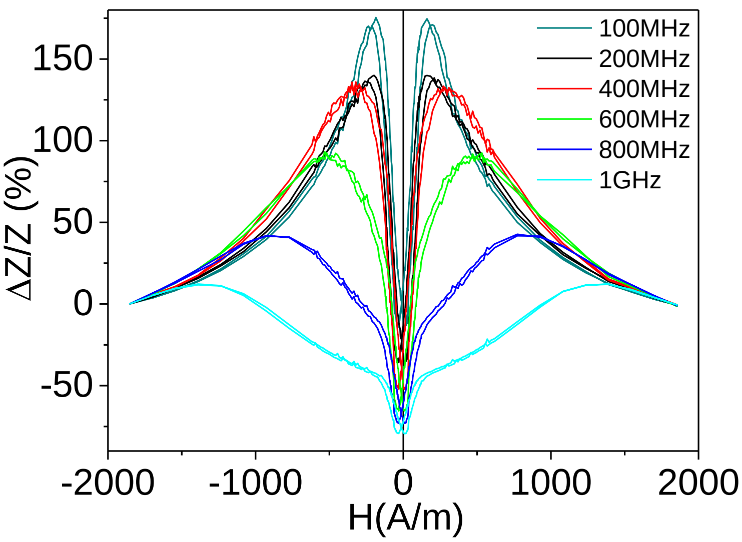

Fig.6. *ΔZ/Z(H)* dependences measured in as-prepared $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires (d≈22 μm, D≈24μm).

2. Glass-coated microwires with the same composition ($Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$) with metallic nucleus diameter: d=38 μm, total microwire diameter: D=43.5 μm.

From the hysteresis loops (shown in Fig. 7) of these microwires measured using the flux-metric method, we can see that such microwires present rather similar soft magnetic properties: coercivity, H_c, about 20 A m^{-1} and the magnetic anisotropy field, H_k, about 150 A m^{-1}.

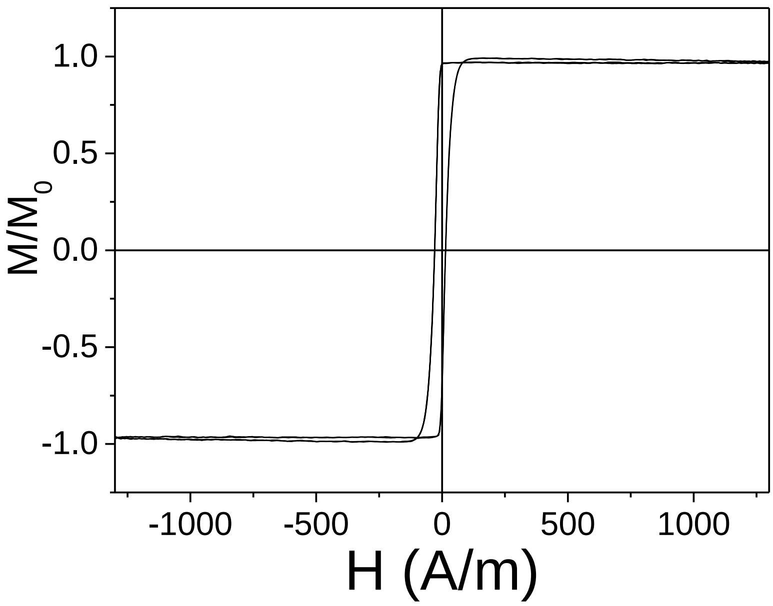

Fig.7. Hysteresis loops as-prepared $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires (d≈38 μm, D≈43.5μm).

From Fig. 8 we can appreciate that these microwires present considerable GMI effect (maximum GMI ratio about 280%).

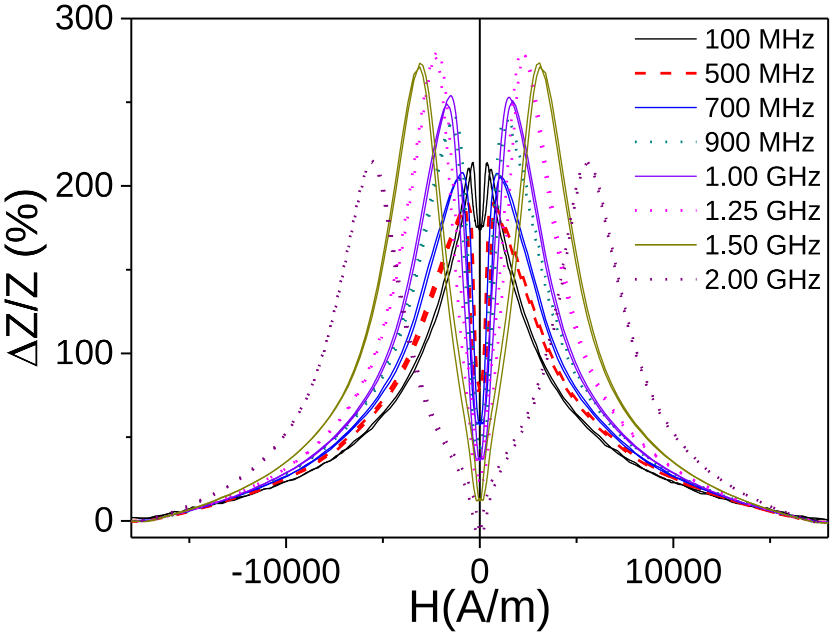

Fig.8. *ΔZ/Z(H)* dependences measured in as-prepared $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires (d≈38 μm, D≈43.5μm).

3. Glass-coated microwires with the composition $Co_{69}Fe_{3.6}Ni_1B_{12.8}Si_{10.7}Mo_{1.5}C_{1.2}$, with metallic nucleus diameter, d=22.8 μm, total microwire diameter: D=23.2 μm. In this case we have tried to prepare the microwires with the thinnest glass-coating (0.2 μm in thickness)

From the hysteresis loops of these microwires provided in Fig. 9.

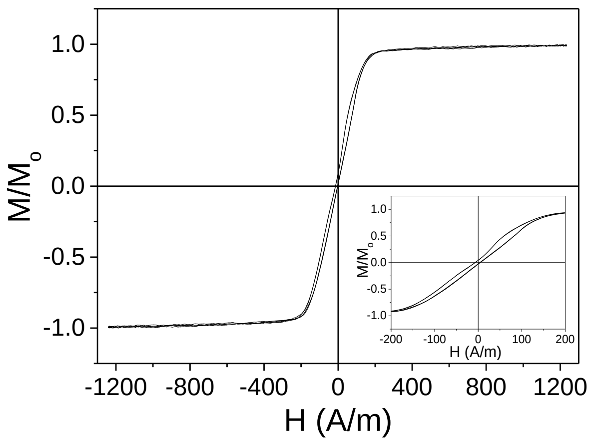

Fig.9. Hysteresis loops of as-prepared $Co_{69}Fe_{3.6}Ni_1B_{12.8}Si_{10.7}Mo_{1.5}C_{1.2}$ microwires (d=22.8 μm, D=23.2 μm).

From Fig.9, the H_c and H_k –values similar to those observed for previous Co-rich microwires are observed (i.e., H_c ≈8 A m^{-1} and H_k ≈150 A m^{-1}).

These microwires present high GMI effect (about 140% maximum GMI ratio) as shown in Fig .10.

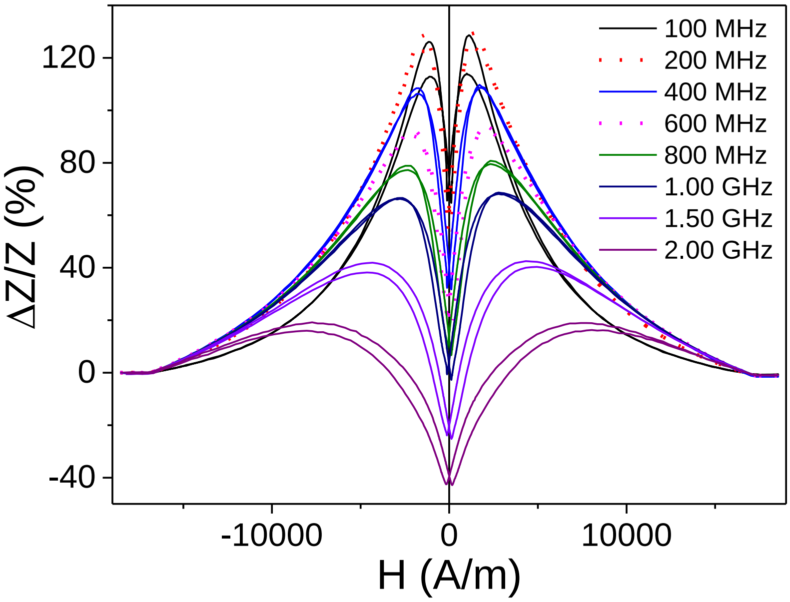

Fig.11. *ΔZ/Z(H)* dependences measured in as-prepared $Co_{69}Fe_{3.6}Ni_1B_{12.8}Si_{10.7}Mo_{1.5}C_{1.2}$ microwires (d=22.8 μm, D=23.2 μm).

Despite very thin glass-coating, maximum GMI ratio, *ΔZ/Zmax,* of these microwires are lower than those of $Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$ microwires.

4. For comparison we prepared and measured magnetic properties and GMI effect in $Fe_{77.5}B_{15}Si_{7.5}$ glass-coated microwires (d=23 μm, D=37 μm).

Hysteresis loops of these microwires (measured using the flux-metric method) are provided in Fig. 11. These microwires present rectangular hysteresis loops, as typically observed in microwires with positive λ_s, values elsewhere [1]. The coercivity, H_c, is about 100 A m^{-1}.

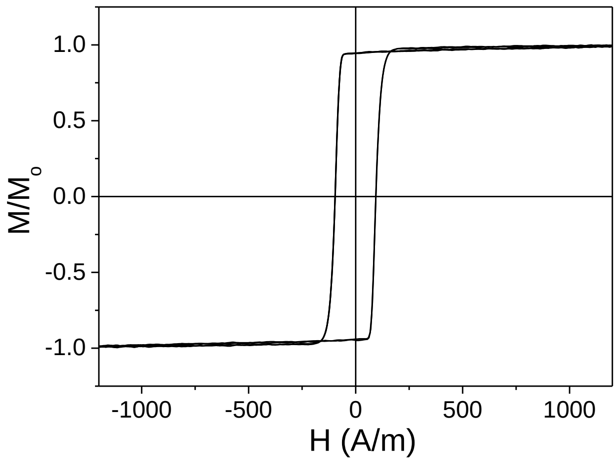

Fig.11. Hysteresis loops as-prepared $Fe_{77.5}B_{15}Si_{7.5}$ microwires (d=23μm, D=37μm).

The GMI effect of these microwires is rather low (*ΔZ/Zmax* below 30%), as can be seen in Fig. 12. Accordingly, at this stage of the project these microwires have been discarded.

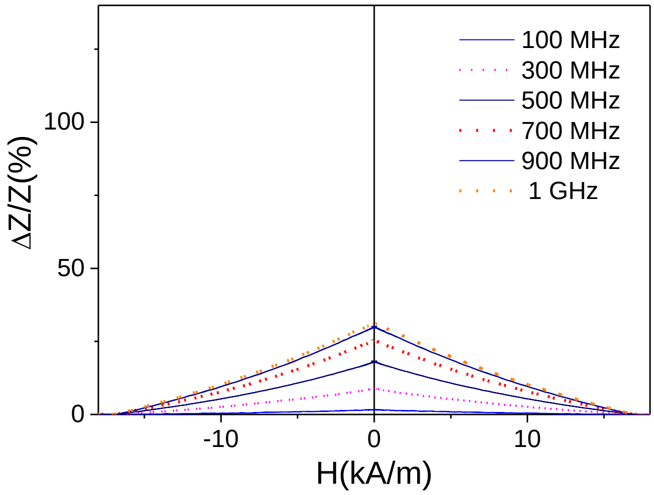

Fig. 12. *ΔZ/Z(H)* dependencies measured in as-prepared $Fe_{77.5}B_{15}Si_{7.5}$ microwires (d=23µm, D=37µm).

The magnetic properties, such as coercivity, magnetic anisotropy field, as well as the GMI ratio of evaluated samples are collected in Table 1.

Table 1. Compositions and properties of microwires produced in Tamag and UPV/EHU and supplied to the different consortia members of INFINITE.

Composition	**Total diameter, D (µm)**	**Metallic nucleus diameter, d (µm)**	**Coercivity (A/m)**	**Magnetic anisotropy field (A/m)**	**Maximum GMI ratio (%)**
$Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$	**43.5**	**38**	**20**	**150**	**280**
$Co_{69}Fe_{3.6}Ni_{1}B_{12.8}Si_{10.7}Mo_{1.5}C_{1.2}$	**23,2**	**22.8**	**8**	**150**	**130**
$Co_{64.6}Fe_{5.0}B_{16.0}Si_{11.0}Cr_{3.4}$	**24**	**22**	**16**	**150**	**175**
$Fe_{77.5}B_{15}Si_{7.5}$	**37**	**23**	**100**		**30**

Accordingly, considering that the necessary condition for the proposed application (composites monitoring) is substantial GMI effect in the ferromagnetic microwires at GHz frequencies, at the first stage of the project we selected Co-rich microwires.

On the other hand, during the project development we have tried to manufacture glass-coated microwires with higher GMI effect.

4. MICROWIRES OPTIMIZATION

With aim of GMI effect improvement, we have prepared new Co-rich microwires.

Although prepared in first step Co-rich microwires present high GMI effect (*ΔZ/Zmax* up to 280 %), these *ΔZ/Zmax* -values are below reported previously *ΔZ/Zmax* –values [1]. Here, we also considered that thicker microwires can have higher magnetic signal. We selected the $Co_{72}Fe_4B_{13}Si_{11}$ composition and thicker metallic nucleus diameter, d, of about 40 µm. It is worth mentioning that commonly considered that the Taylor-Ulitovsky method is suitable for preparation of microwires with d ≤ 30 µm. However, UPV/EHU group together with Tamag recently demonstrated that essentially the same technology can be used for preparation of thicker glass-coated microwires with diameters up to 100 µm [1].

Newly prepared $Co_{72}Fe_4B_{13}Si_{11}$ microwires with d≈40 µm present good magnetic softness (H_k ≈130 A/m, H_c ≈20 A/m) (see Fig. 13) and even most relevant, these microwires present higher GMI effect (see Fig. 14) with maximum GMI ratio up to 600% (among the highest GMI ratio reported up to now).

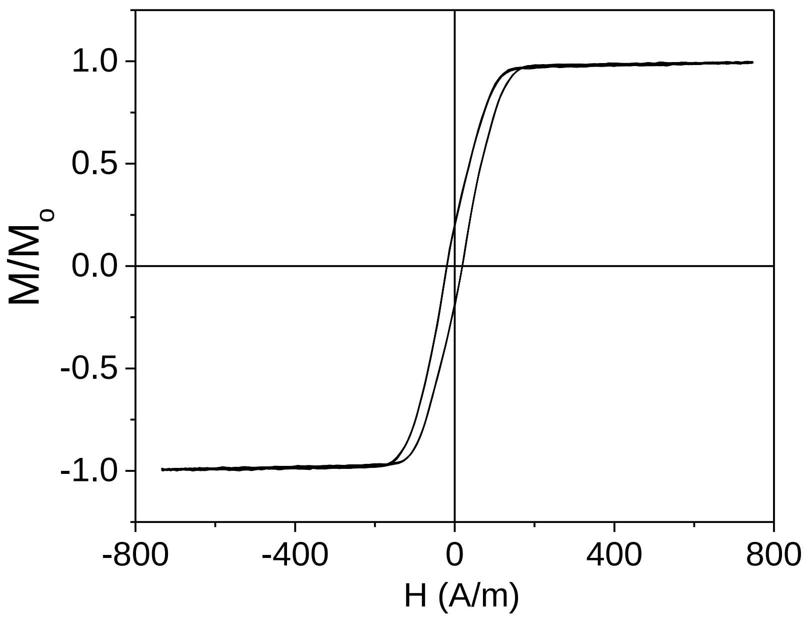

Fig.13. Hysteresis loops as-prepared $Co_{72}Fe_4B_{13}Si_{11}$ microwires (d=40 µm, D=45 µm).

Considering better *ΔZ/Zmax* –values obtained in $Co_{72}Fe_4B_{13}Si_{11}$ microwires, we proposed to use such microwires for the coupons preparation. Accordingly in manufacturing facilities of Tamag we have manufactured about 10 km of $Co_{72}Fe_4B_{13}Si_{11}$ microwires. All the manufactured $Co_{72}Fe_4B_{13}Si_{11}$ microwires present excellent soft magnetic properties (H_k ≈130 A/m, H_c ≈20 A/m) and among the highest *ΔZ/Zmax* –values (up to 600 %).

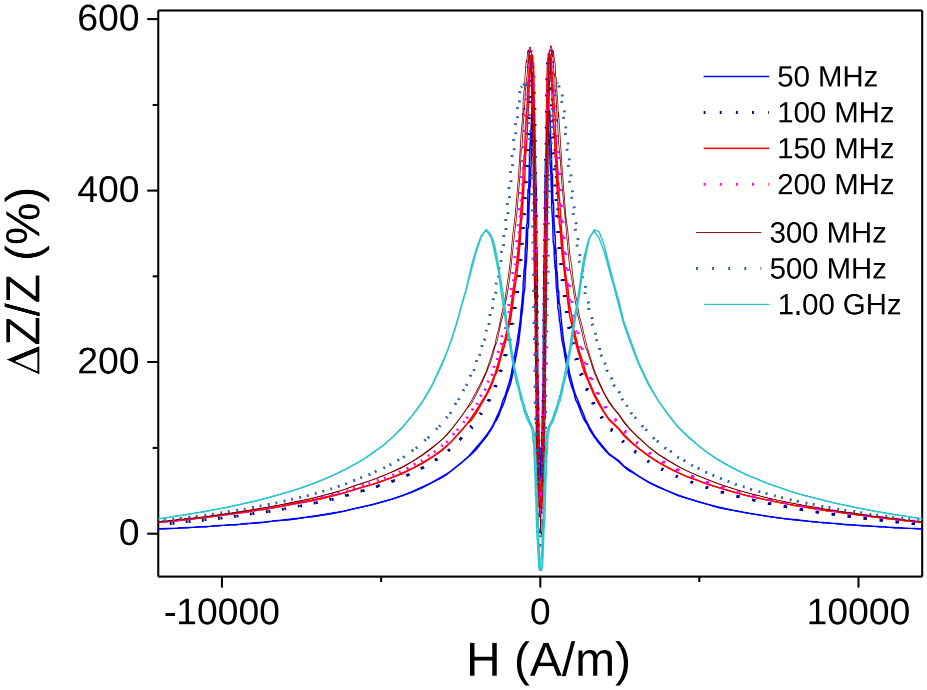

Fig.14. *ΔZ/Z(H)* dependencies measured in as-prepared $Co_{72}Fe_4B_{13}Si_{11}$ microwires (d=40 μm, D=45 μm).

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